ENHANCED ALKALINE HYDROLYSIS AND BIODEGRADABILITY STUDIES OF NITROCELLULOSE-BEARING MISSILE PROPELLANT

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ABSTRACT

Large amounts of energetic materials which have been accumulated over the years in various manufacturing and military installations must be disposed of in an environmentally sound manner. Historically, the method of choice for destruction of obsolete or aging energetic materials has been open burning or open detonation (OB/OD). This destruction approach has become undesirable due to air pollution problems. Therefore, there is a need for new technologies which will effectively and economically deal with the disposal of energetic materials. Along those lines, we have investigated a chemical/biological process for the safe destruction and disposal of a double base solid rocket propellant (AHH), which was used in several 8 inch projectile systems. The solid propellant is made of nitrocellulose and nitroglycerin as energetic components, two lead salts which act as ballistic modifiers, triacetin as a plasticizer and 2-Nitrodiphenylamine (2-NDPA) as a stabilizer. A process train is being developed to convert the organic components of the propellant to biodegradable products and remove the lead from the process stream. The solid propellant is first hydrolyzed through an enhanced alkaline hydrolysis process step. Following lead removal and neutralization, the digested liquor rich in nitrates and nitrites is found to be easily biodegradable. The digestion rate of the intact ground propellant as well as the release of nitrite and nitrate groups were substantially increased when ultrasound were supplied to the alkaline reaction medium compared to the conventional alkaline hydrolysis. The effects of reaction time, temperature, sodium hydroxide concentration and other relevant parameters on the digestion efficiency and biodegradability have been studied. The present work indicates that the AHH propellant can be disposed of safely with a combination of physicochemical and biological processes.

C-2

INTRODUCTION

Significant quantities of energetic materials (rocket motor propellants, propellant charges, etc.) have been generated as part of the US. Army demilitarization program. Energetic materials are classified as reactive (40 CFR §261.21) and are listed under the Resource Conservation & Recovery Act (RCRA). This RCRA classification designates energetic materials as a hazardous waste. Historically, the method of choice for destruction of obsolete or aging energetic materials has been open burning or open detonation (OB/OD). This treatment approach has become restrictive over the past several years due to the promulgation of legislation to manage the handling and treatment of hazardous materials.

The goal of the present study is to develop a treatment process and ultimately a pilot scale demonstration facility for AHH. The AHH formulation is used in several 8 inch projectile systems. The Army currently plans to eliminate the 8 inch weapon systems by the FY98. Ultimately, the processes developed as a result of this study could be applied to a significant quantity of AHH propellant from the demilitarization of 8 inch projectiles. Moreover, it is anticipated that a considerable amount of information obtained from the AHH studies will establish the basis for broader application of the technology. Optimization of these chemical/biological treatment systems could provide a viable means of safe and cost effective disposal for a broad array of energetic materials. The compelling benefits from the development of an innovative bioremediation technology are numerous. This technology would significantly reduce disposal and remediation costs of toxic and hazardous components facing both defense and manufacturing communities. In addition this technology could be utilized for a variety of applications, including, but not limited to the destruction of hazardous manufacturing wastes, excess military munitions, and treatment of contaminated soils and waters.

APPROACH

The composition of AHH, a double-base propellant is given in Table 1. Nitroglycerin and nitrocellulose are the energetic components. Triacetin is a plasticizer used to convert nitrocellulose from its natural fibrous state into a gel state required during the mixing and casting fabrication process of the propellant. Triacetin also acts as a desensitizer and prevents the formation of neat nitroglycerin. 2-NDPA is added as a stabilizer to prevent the auto catalytic decomposition of the propellant with decomposition products. Finally the lead salts act as ballistic modifiers for the propellant.

TABLE 1: AHH Propellant Composition.

Component	Wt % Composition
Nitrocellulose	53.9 min.
Nitroglycerin	31.6 nom.
Triacetin	8.8 nom.
2-Nitrodiphenylamine (2-NDPA)	0.9 min.
Lead Salicylate	1.2 nom.
Lead 2-Ethyl Hexoate	2.0 nom.

Bioremediation has been proven effective in the transformation and complete mineralization of some energetic compounds. Simply stated, bioconversions are chemical transformations (reactions) of organic compounds catalyzed by specific enzymes synthesized by microorganisms. It is generally assumed that access to the active site of an enzyme is available only to compounds dissolved or dispersed in the reaction medium. The propellant itself is highly insoluble in water and it must be pre-treated with solvent(s) in order to increase its solubility[1,2]. However the use of solvents introduce an additional component in the system that has to be removed or treated later in the process. Most solvents are toxic to microorganisms when there are present at concentrations that exceed a specific threshold limit. Therefore, this approach limits the amount of solvent that can be used and the incoming stream must be diluted, to minimize adverse effects on the biomass, which will increase the overall volume of the waste stream. Another technique which can be used when the substrate does not suit the desired bioconversion is to carry out first a chemical modification of the substrate. For example, the alkaline hydrolysis of nitrocellulose has been shown to provide a useful mean to degrade chemically the water insoluble nitrocellulose[3,4]. This alkaline hydrolysis process results in complete digestion of nitrocellulose. Kenyon and Gray[4] documented the presence of a wide variety of organic and inorganic products resulting from the alkaline digestion of nitrocellulose such as nitrates, nitrites, ammonia, cyanide, malic, oxalic, glycolic, trioxyglutaric, dioxybutyric, malonic, tartonic and other unidentified complex acids, sugars, modified celluloses and their nitrates, and partially denitrated cellulose nitrate. Wendt and Kaplan[3], reported that after neutralization, dilution to control nitrate levels and addition of a suitable carbon source (glucose) the digested nitrocellulose liquor is biodegradable. Alkaline decomposition of nitroglycerin produces ammonia, carbon dioxide, formic acid, acetic acid, alkali nitrates, alkali nitrites and intermediate peroxides according to Kenyon and Gray[4]. In the present work, the effect of ultrasound on the alkaline digestion of the AHH propellant has been explored.

The treatment process train tested for the destruction of AHH is illustrated in Figure 1. The propellant is ground and digested in sodium hydroxide solutions, the lead is removed by chemical precipitation and finally the resultant solution, which is rich in organic carbon and nitrogen, is treated biologically to remove carbonaceous and nitrogenous BOD. The final selection of the most suitable option will depend on the kinetics and stoichiometry of the denitrification of the digested propellant and the biological capabilities of nearby wastewater sewage treatment plant. In addition to the alkaline hydrolysis of the propellant mixture, the hydrolysis of pure nitrocellulose was investigated in order to compare the nitrogen releases in the two systems.
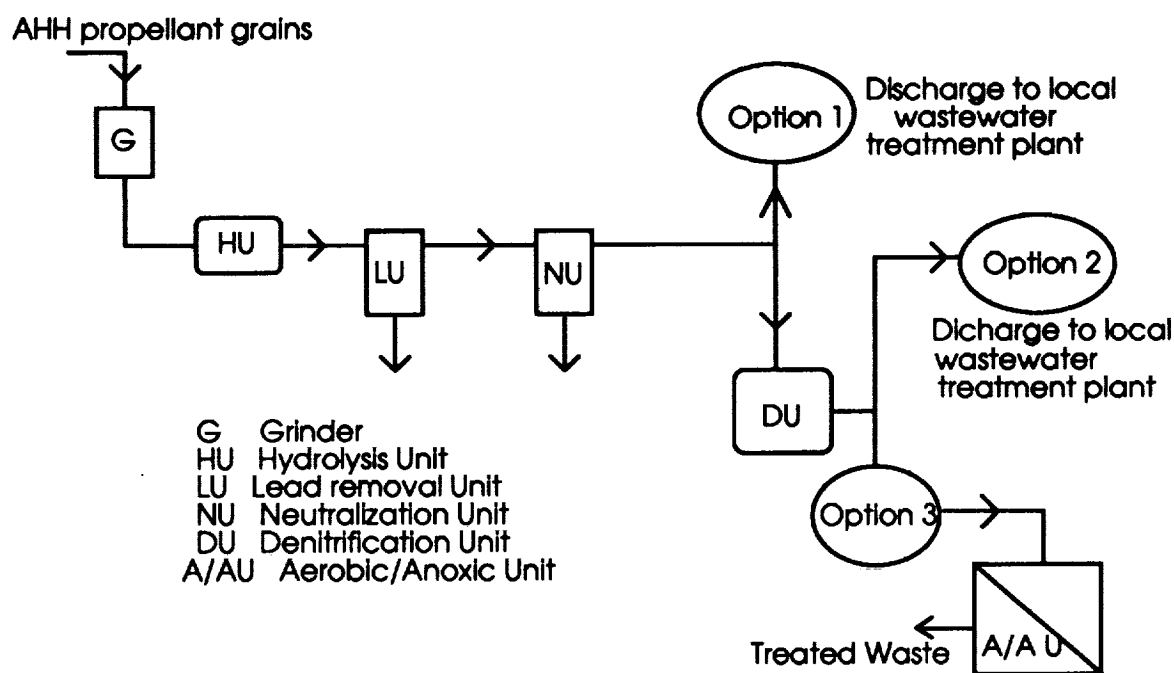
AHH propellant grains

FIGURE 1: Synoptic Diagram for the AHH Propellant Treatment Process

EQUIPMENT AND METHODS

Pure nitrocellulose containing approximately 12.2% nitrogen was obtained from Aqualon, a division of Hercules Incorporated. AHH propellant samples were supplied by Picatinny Arsenal personnel. A sample was prepared from a war reserve M753 rocket motor downloaded at Picatinny Arsenal in 1992. The motor was disassembled per FSAC standard operation procedures. The irregular shaped grain segment was inserted horizontally in the bed of a lathe chuck. Without cutting fluid, a one inch hole was bored in the base of the grain segment. The resulting shavings were collected and stored under environmentally controlled conditions. Next, a grinder (Thomas Wiley Intermediate Mill) was used to process the shavings into 20 Mesh size granules. No fluids were introduced during this operation.

The digestion of the solid propellant and nitrocellulose was carried out in Erlenmeyer flasks. Approximately 0.5 grams of solids were added to fifty milliliters (50 mL) of aqueous sodium hydroxide solution in a 100 mL flasks. This resulted in 1% by weight solids mixture. The flasks were immersed in a sonicator equipped with a water bath capable of maintaining a maximum temperature of 95°C. · The sonicator (Fisher Scientific, Model FS14) had a constant power output of 270 watts and 43kHz frequency. In a typical experiment at a given temperature and sodium hydroxide concentration, the alkaline hydrolysis was carried out for 30 to 60 minutes. After digestion the solution was cooled to room temperature and prepared for precipitation of lead by pH adjustments, and sodium sulfide addition. The pH of the decomposition mixture was adjusted with sulfuric acid. Upon removal of lead, the BOD and COD of the mixture were

90

determined. The lead free supernatant solution, rich in carbon and nitrogen, was neutralized and passed through an acclimated denitrification reactor.

The nitrite and nitrate concentrations were determined by direct injection of collected aliquots using High Pressure Liquid Chromatography (HPLC) on a Varian LC Workstation equipped with a diode array detector, and a Universal Anion 4.6×150 mm, 5μm (Alltech Associates Inc., Deerfield, IL) chromatographic column. Total Kjeldahl Nitrogen (TKN), a measure of nitrogen in the trinegative state, was determined according to Standard Methods[5]. Ammonia was measured by an ammonia selective electrode[5]. Measurements of BOD and COD were also performed following Standard Methods[5] procedures. The concentration of lead in the digestion liquor was determined by Atomic Absorption using a Varian Zeeman 400 Graphite Furnace equipped with an autosampler.

RESULTS AND DISCUSSION

Alkaline Hydrolysis

The effects of reaction time, temperature, and sodium hydroxide concentration on the digestion efficiency were examined. Digestion experiments were carried out at 35, 45, 55, 65, 75, 85 and 95°C in different sodium hydroxide solutions ranging from 2 to 15 % by weight. The sonication power was kept constant and no mechanical mixing was provided. Results for three sodium hydroxide concentrations are presented in Figure 2. The percent digestion is defined as $[(m_i-m_f)/m_i] \cdot 100$ where m_i and m_f are the initial and final mass of solid propellant respectively. Figure 2 shows that the digestion efficiency increases with temperature and sodium hydroxide concentration.
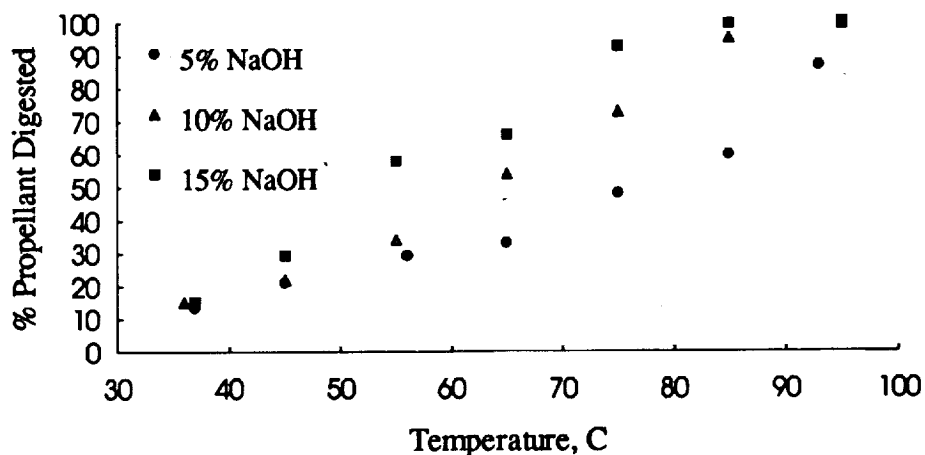

FIGURE 2: Digestion of AHH at Various NaOH Concentrations and Reaction Temperatures.

Experiments were also performed with mechanical agitation of the reaction medium and a combination of sonication and mechanical mixing. Mechanical agitation resulted in significant increases of the digestion rates, at all temperatures, over the rates obtained by sonication alone. However, combination of sonication and mechanical agitation produced higher digestion rates

than sonication or mixing alone. For instance, in an experiment conducted at 90°C with 0.25g AHH in 50 ml 2 wt% NaOH under well mixed conditions for 1 hour the observed digestion was 78.82%. When the experiment was repeated with the sonicator turned on, 84.80% of the propellant was hydrolyzed. Data presented in Table 2 correspond to another typical experiment conducted with 0.5 g AHH in 50 ml 2 wt% NaOH solution.. Although the results indicate that a significant increase in digestion rate and total nitrogen release, this may not be sufficiently high to justify the costs associated with the installation of large sonicators in a full-scale system. Therefore, the economic advantages of sonication must be carefully examined. It should be noted that sonication power requirements can be significantly reduced by intermittent application of ultrasound[6].

TABLE 2: Effect of reaction type on alkaline digestion of AHH propellant

Reaction type	Digestion wt %	[NO⁻₂] ppm	[NO⁻₃] ppm	Total N ppm
Good Mixing and no sonication	56.73	1522.80	1014.30	665.50
Sonication plus "poor mixing"	64.78	1630.20	1100.00	744.55
Sonication plus "good mixing"	77.79	2038.30	1427.80	942.76

The nitrogen released from the decomposition of AHH was compared to nitrogen released by alkaline hydrolysis of NC under identical experimental conditions. The results obtained from the alkaline hydrolysis of AHH and pure NC are presented below.

Experiments at 90°C with varying alkali to propellant ratio and sonication were carried out using 50 mL NaOH solutions and 0.5 grams of ground propellant with sonication only. The nitrate and nitrite production was monitored during the course of the reaction and is presented in Figure 3 for different NaOH concentrations. The total nitrogen produced in the forms of nitrate and nitrite is proportional to the amount of propellant digested and appears to be independent of NaOH concentration. The ratio of nitrite to nitrate is approximately 2 to 1 regardless of the degree of digestion. The theoretical amount of nitrogen in solution containing 1% solids, based on the nominal propellant composition and assuming 13.5% nitration of cellulose, is about 1312 mg/L. In a typical experiment at 97.50 % digestion of the propellant 768.33 mg/L of nitrite-N, and 385.23 mg/L of nitrate-N, were released. Approximately 60 % of the original nitrate groups were reduced to nitrite. The total nitrogen produced as nitrate and nitrite accounts for 90.12 % of the nitrogen originally present in the propellant.

The nitrite and nitrate measurements indicated that about 10% of the original nitrogen was unaccounted and apparently bound to post-degradation organic carbon residuals. In an attempt to close the nitrogen mass balance we performed TKN measurements of the digested liquor. The TKN was found to be about 23 mg/L or 1.8 % of the original nitrogen. Ammonia was also a product of decomposition and was detected in solution at a concentration of 0.5 mg/L as NH_3-N. However, most of the ammonia formed was probably stripped-off due to the strong basic environment which shifts the acid-base equilibrium reaction in favor of ammonia formation. Cyanide, another degradation product, could combine with hydronium ions to form the volatile hydrocyanic acid. Ammonia and small amounts of cyanide may account for the missing 10% of original nitrogen. Considering that nominal compositions of nitrocellulose and nitroglycerin were

used to compute the total expected nitrogen in the propellant, and the heterogeneity of the samples used during digestion, the nitrogen mass balance is quite satisfactory.

NC decomposition was studied at 90°C with varying alkali to nitrocellulose ratio and sonication by preparing 1% solids solutions and various NaOH strengths. The degree of digestion and the concentrations of nitrite and nitrate were monitored for one hour reaction time. Typical results of NC hydrolysis are illustrated in Figure 4. Pure NC appears to degrade faster than the AHH formulation and 100% digestion is achieved within one hour at 2% NaOH dosage. The ratio of nitrite-N to nitrate-N is approximately 2.8 regardless of the degree of digestion. This finding is in good agreement with the results obtained by Kenyon and Gray[4] who found 0.075 mole of nitrite and 0.025 mole of nitrate per liter of alkaline decomposition mixture. Moreover, the independence of this ratio from the degree of digestion suggests that the hydrolysis of nitrocellulose and nitroglycerin is a single step process where nitrates and nitrites are formed directly from the cleavage of the parent molecules. Wendt and Kaplan[3] also demonstrated that the decomposition of NC in alkaline environments proceeds in a single step, by determination of the nitrogen, carbon and oxygen contained in the residual (undigested) NC during the course of the reaction.
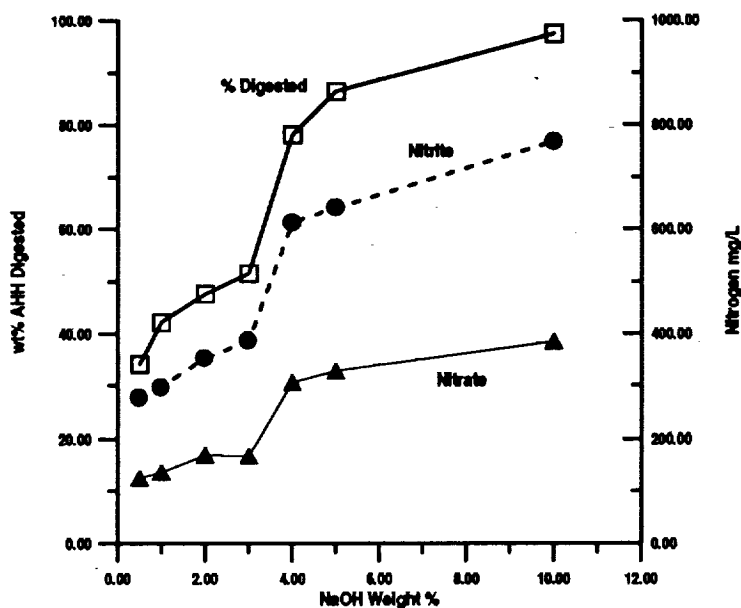

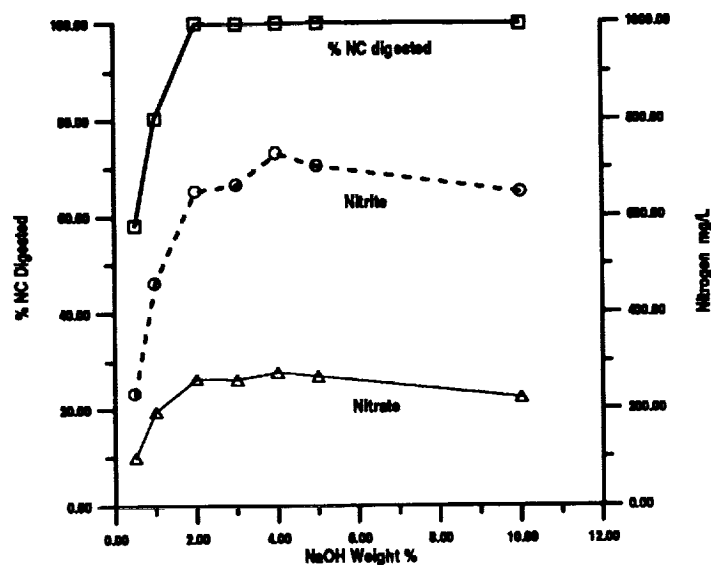FIGURE 3: Nitrate and Nitrite Release During AHH Decomposition

FIGURE 4: Nitrate and Nitrite Release During NC Decomposition

The theoretical amount of nitrogen in a 1% NC solids (12.2% nitration) mixture is 1220 mg/L. The conversion of the original nitrate-N to nitrite-N is about 80%. The TKN of the decomposition mixture was found to be 116 mg/L or 9.5% of the original nitrogen. The total amount of nitrogen accounted for in the forms of nitrate, nitrite and TKN is 89.5 %. Loses of ammonia and HCN, which are known decomposition products, from the system may account for portion of the remaining 10.5% of nitrogen. However, no attempt was made to quantify other nitrogen-containing degradation products.

Lead Removal

The propellant contains a substantial amount of lead, approximately 1.6% wt, which must be removed prior to biological treatment of the digestion liquor. The initial total Pb concentration in the digestion liquor ranges from 65 ppm to 70 ppm and at these concentrations it will be highly toxic and inhibitory to microbial growth. Since PbS is highly insoluble in water, it was decided to dose the solution with Na_2S and precipitate lead as PbS. To facilitate precipitation, the pH of the solution was adjusted to the minimum PbS solubility. According to the theoretical solubility diagram, PbS exhibits minimal solubility at pH of around 8. After pH adjustments, various amounts of Na_2S are added in order to determine an optimal dosage. The results of a typical experiment are shown in Figure 5. For this particular experiment the initial Pb concentration was 55 ppm. The highest percent removal (99.36) was observed at a sodium sulfite dosage of 1.0 mM. Lead removal may also be facilitated by the formation and co-precipitation of lead sulfate, lead hydroxide and lead carbonate due to the presence of the corresponding anions and pH adjustments.
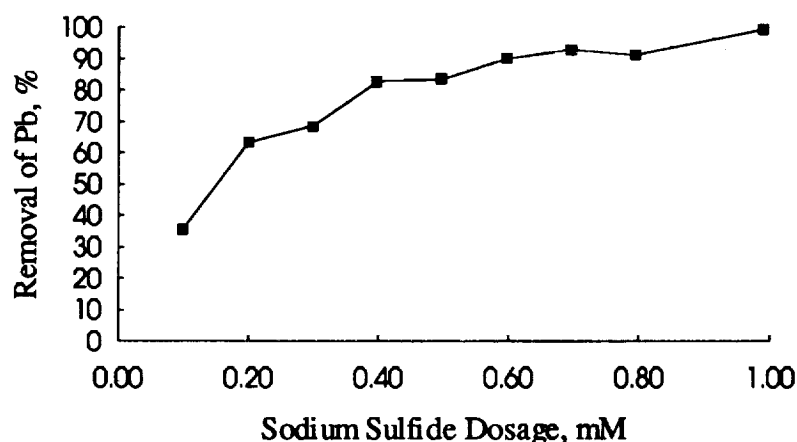
94

FIGURE 5: Lead Removal at Various Sodium Sulfide Concentrations

The solubility of lead sulfide in the presence of the post-degradation organic compounds was investigated in 0.5 mM sodium sulfide solutions and various pH environments. The results are presented in Table 3. Maximum lead removal was observed at pH around 9. Although sodium sulfide is added in excess of stoichiometric requirements for total lead precipitation, it appears that the precipitation process is greatly affected by the formation of lead complexes. A solubility diagram was constructed for this system and compared with the theoretical pC-pH diagram for PbS. This comparison showed that the solubility of Pb was much higher than that predicted by theoretical considerations and suggests the formation of organo-lead complexes which substantially increase the solubility of lead.

TABLE 3: pH Effects on Lead Removal by Sodium Sulfide Precipitation at 0.5 mM.

Final pH	Initial Lead Concentration [ppm]	Final Lead Concentration [ppm]	Lead Removal (%)
6.50	67.41	7.75	88.50
6.58	59.77	13.63	77.66
7.36	62.79	5.55	91.16
7.97	63.19	6.38	89.90
8.18	64.93	7.65	88.22
8.43	54.14	5.48	89.88
8.72	53.59	3.62	93.24
9.02	35.26	2.10	94.06
9.17	21.00	4.74	77.44
10.00	11.03	2.37	78.56
10.41	15.59	4.19	73.15
11.73	52.02	8.76	83.17

Five days biological oxygen demand tests were carried out directly with the neutralized digested propellant. The average BOD and COD of three samples before lead removal were 1480 mg/L and 2960 mg/L respectively. After lead removal the BOD and COD were found to be 435 mg/L and 2295 mg/L respectively.

Denitrification

The BOD and COD results reported above, indicate that the neutralized digested propellant is biodegradable. Since the digested liquor is very rich in nitrates and nitrites, anoxic denitrification experiments were conducted with lead-free digested liquid, to convert them to nitrogen gas. Results showed complete conversion of nitrate and nitrite to nitrogen gas in an acclimated reactor without addition of external carbon source within 30 hours with mixed cultures that have been acclimated for two months. This acclimation period was necessary because it was observed that high initial shock loads of nitrite were inhibitory. In a typical experiment, initial nitrite and nitrate concentrations of 123.3 mg/L and 90.5 mg/L respectively were reduced completely to nitrogen gas within 30 hours.. The initial COD in the reactor was 1274 mg/L and after total nitrite and nitrate conversion, 1168 mg/L of COD were remaining in the system. The COD consumed per unit mass of nitrogen (2 mg COD/mg nitrogen) is close to the values reported in the literature[7]. The complete conversion of nitrite and nitrate and a residual BOD of 94 mg/L in the system prove conclusively that external carbon sources are not necessary for denitrification of the digested propellant. Since BOD is present in excess of the amount required for nitrite and nitrate conversion an additional step is required for complete mineralization of the hydrolysis products. In another set of experiments, fresh activated sludge obtained from a nearby sewage treatment plant was added to the reactor by replacing 1 liter of the prevailing acclimated mixed culture. Following a short acclimation period of 4 days, 135 ml of lead free digested propellant was added to the 2 L reaction volume. The pH was maintained slightly above 7, the agitation speed was 250 rpm and the temperature of the reaction medium was maintained at 30 °C. Results of the time course of the reaction are shown in Figure 6. The results indicate that nitrite is reduced more rapidly than the nitrate. COD measurements indicate that in this case 2.63 mg COD were consumed per mg of nitrogen. The TSS was 1180 mg/L. The difference with the COD/N ratio of 2 reported above might be attributed to cell synthesis since one liter of acclimated mixture culture (acclimated for two months) was replaced by fresh activated mixed culture.
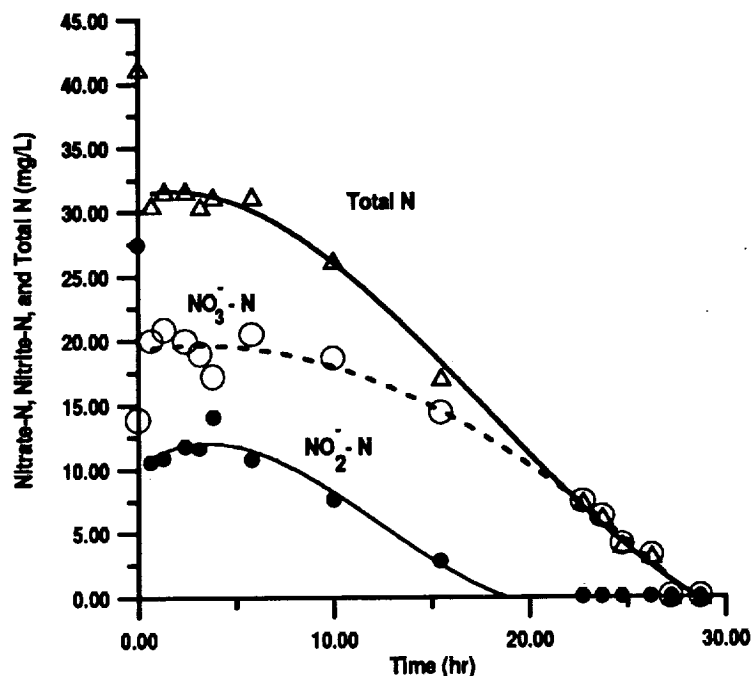
FIGURE 6: Time History of Nitrogen Reduction Under Anoxic Environment

CONCLUSIONS

Simultaneous mixing and sonication appear to significantly enhance the rates of decomposition of AHH in sodium hydroxide solutions. Alkaline hydrolysis decomposes AHH into biodegradable products that can be treated by conventional biological treatment technologies. Approximately 60% of the original nitrate groups of nitrocellulose and nitroglycerin are reduced to nitrite. The amount of nitrogen released in the form of nitrites and nitrates accounts for 90% of the original nitrogen. The remaining 10 % appears to be bound on post-degradation organic carbon or converted to ammonia and other nitrogen compounds. Digestion of nitrocellulose releases 80 % of the original nitrogen as nitrite-N and nitrate-N, and 9.5% as TKN. The lead present in the digestion liquor of the decomposed AHH mixture is effectively removed by precipitation with sodium sulfide. Complexation of lead with organic and inorganic digestion products appears to be responsible for the observed increase in lead solubility. Complete denitrification of the of nitrite and nitrate present in the decomposition mixture is achieved without addition of external carbon sources.

ACKNOWLEDGMENT

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